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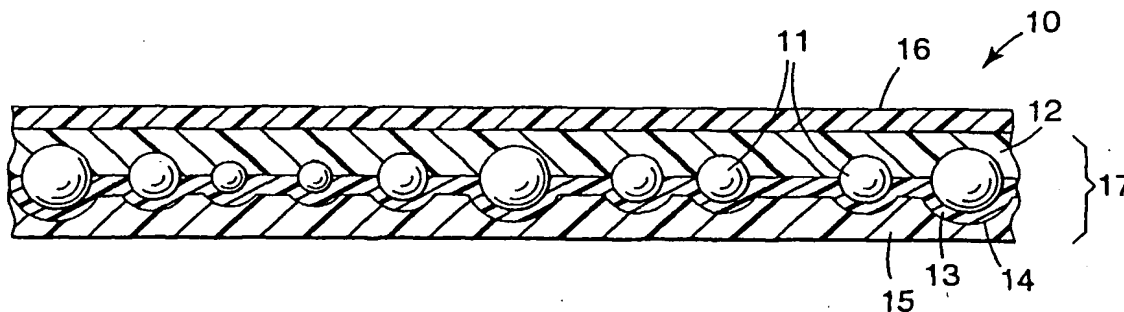
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- (71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).
- (72) Inventors: **WANG, Paul, J.**; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). **HO, Chia-Tie**; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). **NGUYEN, Thanh-Huong, T.**; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). **BAIER, Michael, G.**; Post Office Box 33427, Saint Paul, MN 55133 (US). **HARVEY, Christopher, L.**; Post Office Box 33427, Saint Paul, MN 55133 (US). **KUMAR, Kanta**; P.O. Box 33427, Saint Paul, MN 55133 (US).
- (74) Agents: **GWIN, Doreen, S., L. et al.**; Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).
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(54) Title: SHEETING HAVING AN OPTICAL CORE LAMINATED TO A VINYL FILM, RETROREFLECTIVE ARTICLES, AND METHODS



(57) Abstract: Sheetting, such as retroreflective sheetting, methods of making such sheetting, and articles containing such sheetting. A sheetting includes: a vinyl film having two major surfaces; a preformed optical core laminated to a first major surface of the vinyl film; a primer disposed between the vinyl film and the preformed optical core, wherein the primer includes a urethane polymer; and optionally, graphics positioned between the primer and the optical core or the primer and the vinyl film.

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## SHEETING HAVING AN OPTICAL CORE LAMINATED TO A VINYL FILM, RETROREFLECTIVE ARTICLES, AND METHODS

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### Field of the Invention

The invention relates to retroreflective articles and other articles useful for various applications, such as graphic designs and retroreflective products that include a vinyl film.

10

### Background

Articles containing polymer films have wide utility in such applications as commercial graphics for advertising and for retroreflective products. Specifically, retroreflective products (e.g., bead-based and prismatic-type (e.g. cube corner) retroreflective sheeting) have been developed to provide increased safety, especially during periods of reduced visibility. These articles may encounter demanding environments, such as extremes in temperature, chemical challenges from atmospheric pollution and road salt, and photo-reaction involving infrared, visible, and ultraviolet radiation from sunlight.

One conventional retroreflective base sheeting includes a monolayer of optical elements typically in the form of glass microspheres (i.e., beads) embedded in a polymeric binder layer and a specularly reflective layer covering the polymeric layer. Transparent cover films are used to provide protection (e.g., weather-resistance) to such articles, particularly retroreflective articles such as license plates, signage, and the like. Such cover films have been made by dip coating the base material or by attaching a preformed cover film. For example, preformed cover films can include poly(methyl methacrylate) and poly(ethylene terephthalate). Although these cover films function well when the retroreflective sheeting has a rigid, flat support such as a highway sign, they are not very conformable or stretchable, and thus, not useable for products that require embossing such as license plates. Furthermore, these cover films typically require a pressure sensitive adhesive layer for adhering them to the base sheeting.

Other cover films are known that are more flexible, and thus, useful for products that require embossing. For example, U.S. Pat. No. 4,767,659 (Bailey.

et al.) discloses an extruded thermoplastic film that includes aliphatic urethanes, copolymers of ethylene or propylene, or homopolymers of ethylene and propylene. A preferred cover film includes a copolymer of ethylene and acrylic acid (EAA). Such cover films are extremely effective cover films for  
5 retroreflective sheeting, particularly license plates. One drawback, however, is their poor receptivity to ink-jet and hot foil stamping processes.

Thus, there is a desire to provide retroreflective articles and other articles useful for various applications, such as graphic designs and retroreflective products, that are more receptive to, for example, ink-jet, thermal mass transfer,  
10 and hot foil stamping processes.

### Summary of the Invention

One approach to fulfilling the desire for cover films for retroreflective articles, for example, that are more receptive to printing using ink-jet, thermal  
15 mass transfer, and hot foil stamping processes is to use vinyl films, such as those used in commercial graphics products. However, such vinyl films are not readily bonded to conventional preformed optical cores, which include optical elements such as glass microspheres or prismatic elements. The present invention is directed to a solution to this problem, which involves the use of a primer that  
20 includes a urethane polymer and optionally an olefinic copolymer such as a copolymer of ethylene and acrylic acid (EAA).

Thus, in one embodiment of the present invention, there is provided a sheeting (preferably, retroreflective sheeting) that includes: a vinyl film having two major surfaces; a preformed optical core laminated to a first major surface of  
25 the vinyl film; and a primer disposed between the vinyl film and the preformed optical core, preferably at a (dry) thickness of no greater than about 12.5 micrometers, wherein the primer includes a urethane polymer; and optionally, graphics positioned between the primer and the optical core or between the primer and the vinyl film.

30 The urethane polymer of the primer can be provided by a water-based urethane resin or a solvent-based urethane resin. For embodiments in which the urethane is mixed with an olefinic copolymer such as an EAA copolymer, a

water-based urethane resin is typically used. Typically, the urethane polymer has a weight average molecular weight of about 8000 to about 500,000.

For certain preferred embodiments, the primer also includes a copolymer of an olefinic monomer and a second monomer containing a pendant carboxyl group, such as an ethylene/acrylic acid (EAA) copolymer. This can be mixed (e.g., blended) with the urethane polymer (typically, which is formed from a water-based urethane resin). Alternatively, the primer can include two distinct layers, for example, one of the urethane polymer and one of the EAA copolymer. A mixture (e.g., blend) of urethane polymer and EAA copolymer, for example, can also be used in a primer that includes several layers (typically, two layers). In a preferred mixture of the urethane polymer and olefinic copolymer, an olefinic copolymer is present in an amount of about 7 weight percent (wt-%) to about 87 wt-%, based on polymer solids, and a urethane polymer is present in an amount of about 13 wt-% to about 93 wt-%, based on polymer solids. Whether used in mixtures or in layers, a urethane polymer is preferably proximate the vinyl film.

In another embodiment of the invention, there is provided a sheeting (preferably, a retroreflective sheeting) that includes: a vinyl film having two major surfaces; a preformed optical core laminated to a first major surface of the vinyl film; a primer disposed between the vinyl film and the preformed optical core, wherein the primer consists essentially of a urethane polymer; and optionally, graphics positioned between the primer and the optical core or between the primer and the vinyl film.

In still another embodiment of the invention, there is provided a sheeting (preferably, a retroreflective sheeting) that includes: a vinyl film having two major surfaces; a preformed optical core laminated to a first major surface of the vinyl film; a primer disposed between the vinyl film and the preformed optical core, wherein the primer includes a first layer that includes a urethane polymer proximate the vinyl film and a second layer that includes an ethylene/acrylic acid copolymer; and optionally, graphics positioned between the primer and the optical core or between the primer and the vinyl film. Preferably, either or both layers can include a mixture of an ethylene/acrylic acid copolymer and a urethane polymer.

In a further embodiment, there is provided a sheeting (preferably, a retroreflective sheeting) that includes: a vinyl film having two major surfaces; a preformed optical core laminated to a first major surface of the vinyl film; a primer disposed between the vinyl film and the preformed optical core, wherein  
5 the primer is formed from a solvent-based urethane resin; and optionally, graphics positioned between the primer and the optical core or between the primer and the vinyl film.

In another embodiment, the present invention provides a retroreflective sheeting that includes: a vinyl film having two major surfaces; a preformed  
10 optical core laminated to a first major surface of the vinyl film; a primer disposed between the vinyl film and the preformed optical core at a thickness of no greater than about 12.5 micrometers, wherein the primer includes a urethane polymer; and optionally, graphics positioned between the primer and the optical core or between the primer and the vinyl film.

15 The present invention also provides methods of making such sheeting (preferably, retroreflective sheeting). In general, these methods involve laminating a vinyl film to a preformed optical core. The vinyl film, the preformed optical core, or both are primed with a primer that includes a urethane primer before laminating them together. Also, graphics can optionally be applied  
20 to the vinyl film, the preformed optical core, or both prior to lamination.

In one preferred embodiment, a method is provided that includes: providing a vinyl film that includes a primer disposed on a first major surface thereof to form a primed surface, wherein the primer includes a urethane polymer; providing a preformed optical core having two major surfaces; and  
25 laminating a first major surface of the preformed optical core to the primed surface of the vinyl film. In this method, the vinyl film can be primed with a urethane polymer provided from a water-based urethane resin or from a solvent-based urethane resin.

In another preferred embodiment, a method is provided that includes:  
30 providing a vinyl film having two major surfaces; providing a preformed optical core that includes a primer disposed on a first major surface thereof to form a primed surface, wherein the primer includes a urethane polymer; and laminating a first major surface of the vinyl film to the primed surface of the preformed

optical core. In this method, the optical core is preferably primed with a urethane polymer provided from a water-based urethane resin.

As discussed above for the sheeting, the primer used in the methods can also include an olefinic copolymer such as an ethylene/acrylic acid (EAA) copolymer. This can be mixed (e.g., blended) with the urethane polymer (typically, which is formed from a water-based urethane resin). Alternatively, the primer can include two distinct layers – one of the urethane polymer and one of the olefinic copolymer, as long as the urethane polymer is proximate the vinyl film.

10 In all the embodiments described herein, a preformed optical core includes optical elements typically in the form of glass microspheres (i.e., beads) or prisms, for example. Microspheres can be embedded in a polymeric binder layer or pressed into a polymeric film, for example. Such preformed optical cores are well known to those of skill in the art.

15 The sheeting of the present invention can be used in a variety of products, including, but not limited to, license plates, reflective graphic articles, and pavement markings.

As used herein, the phrase "urethane polymer" refers to a urethane-containing polymer or copolymer. Such materials may alternatively be referred to as a "polyurethane." The term "polyurethane" typically includes polymers having urethane and/or urea linkages, and such is the intended meaning herein.

As used herein, the phrase "primer" or "primer layer" refers to a layer that adheres two or more other layers, films, and/or sheets to each other, usually when these would not sufficiently adhere to each other absent the primer therebetween.

### **Brief Description of the Drawings**

The invention will be further explained with reference to the drawings, wherein:

- 5           Fig. 1 is a cross-sectional view of an embedded-lens retroreflective article;
- Fig. 2 is a cross-sectional view of an enclosed-lens retroreflective article;
- Fig. 3 is a cross-sectional view of an alternative embodiment of an enclosed-lens retroreflective article;
- 10          Fig. 4 is a cross-sectional view of an encapsulated-lens retroreflective article;
- Fig. 5a is a cross-sectional view of an exposed prismatic-type retroreflective article;
- Fig. 5b is a cross-sectional view of an enclosed prismatic-type
- 15   retroreflective article; and
- Fig. 6 is a cross-sectional view of an encapsulated prismatic-type retroreflective article.

These figures, which are idealized, are not to scale and are intended to be merely illustrative and non-limiting.

20

### **Detailed Description of Preferred Embodiments**

The present invention provides sheeting (preferably, retroreflective sheeting) that includes a vinyl film having two major surfaces and a preformed optical core in the form of a sheet material laminated to a first major surface of

25   the vinyl film. Significantly, a primer that includes a urethane polymer is used to enhance the adhesion of the vinyl film laminated to the preformed optical core.

Preferably, the primer is present at a dry coating thickness of no greater than about 12.5 micrometers, more preferably no greater than about 6 micrometers, and most preferably no greater than about 5 micrometers.

30   Preferably, suitable bonding of an optical core to a vinyl film occurs if the peel force using the 180° peel test described in the Examples Section is at least about 356 grams/centimeter (g/cm) (2.0 pounds/inch (lb/in)), preferably, at least about 455 g/cm (2.5 lb/in), and more preferably, at least about 535 g/cm (3.0 lb/in).

Generally, in retroreflective articles, a preformed optical core can include a monolayer of optical elements typically in the form of glass microspheres (i.e., beads). These microspheres can be embedded in a polymeric binder layer or pressed into a polymeric film, for example. Alternatively, a preformed optical  
5 core can include prismatic-type optical elements. Such preformed optical cores (i.e., optical core sheets) are well known to those of skill in the art. Preferably, the optical core is an enclosed-lens optical core or an embedded-lens optical core.

Generally, in retroreflective articles, the vinyl film forms the first major  
10 viewing surface of a retroreflective article. It is often called the face member, overlay, cover film, top film, front face, top layer, or top coat, which for the purposes of this application are all equivalent terms. Suitable cover films provide a substantially transparent viewing surface that protects the optical elements from a variety of possible destructive effects, such as dirt, water, and  
15 exposure to weather and outdoor conditions. Polymers selected for the cover films are preferably dimensionally stable, durable, weatherable, and readily formable into a desired configuration. Herein, the vinyl cover film is also receptive to inks used in ink-jet printing processes, hot foil stamping processes, and thermal mass transfer processes, for example.

20

### **Primer**

The primer comprises (and for certain embodiments, consists essentially of) a urethane polymer (i.e., a urethane-containing polymer or copolymer, alternatively referred to as a polyurethane, which includes polymers having  
25 urethane and/or urea linkages).

Preferably, the primer also includes a copolymer of an olefinic monomer and a second monomer containing a pendant carboxyl group (e.g., a compound of Formula I below), such as an ethylene/acrylic acid (EAA) copolymer. This can be mixed (e.g., blended) with the urethane polymer (typically, which is  
30 formed from a water-based urethane resin). Alternatively, the primer can include two distinct layers, for example, one of the urethane polymer and one of the olefinic copolymer. A mixture (e.g., blend) of urethane polymer and olefinic copolymer can also be used in a primer that includes several layers (typically,



two layers). For example, a mixture of urethane polymer and olefinic copolymer can form a first layer proximate the vinyl film with a second layer of either the urethane polymer, the olefinic copolymer, or a mixture of the two. In a preferred mixture of the urethane polymer and olefinic copolymer, an olefinic copolymer  
5 is present in an amount of about 7 wt-% to about 87 wt-%, based on polymer solids, and a urethane polymer is present in an amount of about 13 wt-% to about 93 wt-%, based on polymer solids. Such mixtures are described in U.S. Patent No. 5,468,532 (Ho et al.); however, the primer of the present invention is preferably not crosslinked. Also, the primer of the present invention preferably  
10 does not include colorants. Whether used in mixtures or in layers, a urethane polymer is proximate the vinyl film for desirable adhesion to the optical core.

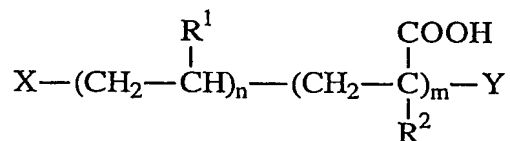
Suitable urethane polymers or copolymers for use in the primer include aliphatic or aromatic urethanes or blends thereof. Preferably, the urethane polymer is an aliphatic urethane. Typically, many suitable polyurethanes include  
15 three main components: an aliphatic or aromatic diisocyanate; a chain extender (such as an ethylene-, propylene- or butane- diol); and a soft segment polyol (such as polyether, polyester, or polycarbonate, e.g., polyethyleneoxide, polyadipate, or polycaprolactone). For water-based urethanes, a water-dispersible segment is also included, such as dimethyl propionic acid or  
20 diethanol amine.

Suitable urethane polymers have a weight average molecular weight of about 8,000 to about 500,000. The urethane polymer of the primer can be provided by a water-based urethane resin or a solvent-based urethane resin. Such urethane resin (dispersions) are commercially available from a variety of sources.  
25 They include aliphatic polyester polyurethanes, aliphatic polyether polyurethanes, aliphatic polycarbonate polyurethanes, and blends thereof.

Examples of suitable dispersion grade urethane polymers include those commercially available from Avecia (formerly Zeneca), Wilmington, MA, under the trade designations "Neorez 972," "Neorez 9679," and "Neorez 960," all of  
30 which are water-based aliphatic polyester urethane resins, and a solvent-based aliphatic polyester urethane resin commercially available from KJ Quinn, Seabrook, NH under the trade designation "QC 4820." For embodiments in

which the urethane is mixed with an EAA copolymer, a water-based urethane resin is typically used.

The primer can also include a copolymer of an olefinic monomer and a second monomer containing a pendant carboxyl group, for better adhesion to the optical core. These olefinic copolymers preferably have the following formula (Formula I):



wherein  $\text{R}^1$  is either H or a  $\text{C}_{1-6}$  alkyl group;  $\text{R}^2$  is H, a  $\text{C}_{1-6}$  alkyl group,  $-\text{CN}$ , an ester group, or  $\text{R}^3-\text{COOH}$ , wherein  $\text{R}^3$  is any alkyl group; X and Y are independently a residue of the olefinic monomer or a residue of the second monomer; n is a number selected such that the olefinic monomer provides from about 70 mole percent (mol-%) to about 99 mol-% of the copolymeric binder; and m is a number selected such that the second monomer correspondingly provides from about 1 mol-% to about 30 mol-% of the copolymeric binder. Preferred such copolymers include copolymerized ethylene and acrylic acid or copolymerized ethylene and methacrylic acid.

Suitable copolymers of ethylene with acrylic acid (EAA) include a dispersion grade EAA commercially available from Michelman Inc., Cincinnati, OH under the trade designation "Michem 4983R." Suitable copolymers of ethylene and methacrylic acid (EMAA) include a dispersion grade EMAA commercially available from Morton International, Seabrook, NH under the trade designation "Adcote 56220."

The primer can optionally include a surfactant (i.e., wetting agent). A sufficient amount of surfactant is typically used such that a uniform coating or film results. Preferably, a primer can include 0 to about 5 wt-% of a surfactant, based upon the total weight of the primer (coatable composition or solution weight). If too much surfactant is included, the resultant laminated sheeting may have poor moisture resistivity, which may also result in poor outdoor durability.

If too little surfactant is included, the primer will not demonstrate sufficient surface wetting upon coating. A surfactant serves to lower the surface tension and improve the coatability of the primer. The surface tension required depends upon the substrate to be coated.

- 5           Useful surfactants for water-based compositions include, but are not limited to, those selected from the group consisting of anionic, nonionic, and cationic surfactants. Preferred surfactants are nonionic. Examples of preferred nonionic surfactants for water-based compositions include, but are not limited to, those selected from the group of ethoxylated tetramethyldecynediol available  
10   from Air Products and Chemicals, Allentown, PA under the trade designation "Surfynol" 440, 420, 465, 104 PA, and 485, and polyether-polysiloxane copolymer commercially available from Tego Chemie Service USA, Hopewell, VA, under the trade designation "Foamex" -800, -805, and -810.

- For non-water-based compositions useful surfactants also include  
15   nonionic surfactants. In general, nonionic surfactants are organic solvent reducible and thus useful in the non-water-based compositions of the invention. Useful nonionic surfactants include, but are not limited to, those selected from the group of cellulose derivatives such as cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate cellulose acetate butyrate butanedioate,  
20   which are commercially available from Eastman Chemical, Kingsport, TN under the trade designations "CAB" -398-3, -381-0.1, -381-0.5, -531.1, and -482-0.5. Numerous other surfactants are commercially available.

- The primer can also include various other additives for desired effect. These include, for example: defoamers, such as that commercially available from  
25   Byk Chemie, Wilmington, DE under the trade designation "Byk 024"; fungicides, such as that commercially available from Troy Chemical, Troy, MI under the trade designation "Troysan Polyphase AF-1"; and ultraviolet protectors, such as hindered amine light stabilizers ("HAL") commercially available from Ciba-Geigy Corp., Greensboro, NC under the trade designation  
30   "Tinuvin 123," and ultraviolet absorbers, commercially available from Ciba-Geigy Corp., Greensboro, NC under the trade designation "Tinuvin 1130."

          The components of the primer, e.g., urethane dispersion, EAA dispersion, and the surfactant, include solvents such as water, isopropanol, and N-methyl

pyrrolidone. If desired, additional water and/or organic solvents can be added to the primer composition to adjust the solids concentration for effective coatability and/or to enhance compatibility of additives. Such organic solvents include alcohols, methyl isobutyl ketone, diisobutyl ketone, xylene, amyl acetate, methyl  
5 amyl acetate, propylene glycol monoethyl ether, or mineral spirits solvent, or combinations thereof. Typically, a suitable solids content for coatability is within a range of about 20 wt-% to about 35 wt-% for primers containing water-based urethane resins and about 10 wt-% to about 15 wt-% for primers containing solvent-based urethane.

10 A preferred coatable primer composition includes 27.9 wt-% "Neorez 972" water-based urethane polymer resin, 65.2 wt-% "Michem 4983R" EAA, 0.5 wt-% "Surfynol 104 PA" surfactant, 0.3 wt-% "Byk 024" defoamer, and 6 wt-% of a solution containing 2.8 wt-% "Troysan Polyphase AF-1" fungicide, 4.2 wt-% "Tinuvin 123" ultraviolet protector, and 12.6 wt-% "Tinuvin 1130" ultraviolet  
15 absorber in 80.4 wt-% propylene glycol monoethyl ether.

The primer can be prepared by mixing the various components and coating onto either the vinyl film or the optical core. Such coating techniques, such as wire bar coating and gravure coating, that are well known to those of skill in the art can be used.

20 Preferably, the primer, whether it includes one layer of more than one layer, has a total thickness once dry of no greater than about 12.5 micrometers. More preferably, the primer, whether in one or more layers, has a total thickness of no greater than about 6 micrometers, and most preferably no greater than about 5 micrometers. Preferably, the thickness is at least about 1 micrometer for  
25 desirable adhesion.

### **Vinyl Film**

A suitable film includes a vinyl-containing plastic film. Herein, "vinyl film" and "vinyl-containing film" are used interchangeably and include those  
30 films having vinyl functionality. The vinyl functionality can be provided by a wide array of polymers, preferably polyvinyl chloride such as that commercially available from Union Carbide, Danbury, CT under the trade designation "Geon 178."

A preferred vinyl film is a transparent vinyl film having a formulation of about 42 wt-% to about 56 wt-% polyvinyl chloride, about 0 to about 25 wt-% acrylic resin, about 15 to about 25 wt-% plasticizers, from about 0.5 wt-% to about 8 wt-% heat stabilizers, and about 0.1 to about 6 wt-% ultraviolet  
5 protectors. Optionally, the vinyl film can include colorants (e.g., dyes or pigments), such as the pigments described in U.S. Patent No. 5,874,158 (Ludwig et al.).

The acrylic resin is preferably included in the vinyl film formulation to provide durability and nonblocking properties. Nonlimiting examples of acrylic  
10 resins include poly(methyl methacrylate) and methyl methacrylate/n-butyl methacrylate copolymer. Suitable acrylic resins are commercially available from Rohn & Haas under the trade designations "Acryloid B66," "Acryloid A11," and "Acryloid A21," and from DuPont under the trade designations "Elvacite 2008," "Elvacite 2010," and "Elvacite 2042."

Nonlimiting examples of ultraviolet protectors include hindered amine  
15 light stabilizers ("HAL") commercially available from Hal-stab Company of Hammond, IN under the trade designations "Hal-Lub," "Hal-Base," "Hal-Carb," and "Hal-Stab"; or from Ciba-Geigy Corp., Greensboro, NC under the trade designation "Tinuvin" (e.g., "Tinuvin 123" and "Tinuvin 292") and ultraviolet  
20 light absorbers such as diphenylacrylate protectors commercially available from BASF of Williamsburg, VA under the trade designation "Uvinul" (e.g., "Univul N-539").

Nonlimiting examples of heat stabilizers include CaZn compounds, such as that commercially available from Witco of Greenwich, CN under the trade  
25 designation "Mark V-1923"; BaZn compounds, such as that commercially available from Ferro Corp., Cleveland, OH under the trade designation "Sympron 940"; BaCdZn compounds, such as that commercially available from Ferro Corp. under the trade designations "Ferro 1237" and "Sympron 856"; and tin mercaptide compounds, such as that commercially available from M&T  
30 Chemicals of Rahway, NJ under the trade designation "Termolite 31."

Nonlimiting examples of plasticizers include dimethyl terephthalate, dimethyl isophthalate, dimethyl octyl terephthalate, and a polyester plasticizer such as that commercially available from Henkel under the trade designation

“Plastolein 9777” (combination of hexanedioic acid, 1,3-butanediol, and 2-ethylhexyl ester).

The vinyl film can be prepared by bar coating on to, for example, a polyester, presized paper, or presized polyester liner, the film formulation in methyl isobutyl ketone, diisobutyl ketone, xylene, amyl acetate, methyl amyl acetate, or mineral spirits solvent. A film having a dry caliper ranging from about 20 micrometers to about 80 micrometers is preferred. Coating involves bar coating of the organosol onto the liner and obtaining the desired film thickness and a smooth, uniform film by placing a smooth, stationary bar at a fixed distance from a moving web substrate.

Examples of suitable vinyl films include those disclosed in U.S. Pat. No. 5,874,158 (Ludwig et al.). Other films are commercially available vinyl films including calendered vinyl from Achilles USA, Everett, WA.

#### 15 **Optical Core**

A preformed optical core includes optical elements typically in the form of glass microspheres (i.e., beads) or prismatic elements, for example. Microspheres can be embedded in a polymeric binder layer or pressed into a polymeric film, for example. Herein, “preformed” means that the optical core was prepared before applying the primer or the vinyl film.

Retroreflective polymeric sheeting in the preferred articles of the present invention may be, for example, “beaded sheeting” in the form of an enclosed-lens sheeting, embedded-lens sheeting, or encapsulated-lens sheeting, as well as cube corner retroreflective sheeting. Such articles are described, for example, in U.S. Pat. Nos. 2,407,680; 4,511,210; 4,950,525; 3,190,178; 4,025,159; 4,896,943; 5,064,272; 5,066,098; 3,684,348; 4,801,193; 4,895,428; and 4,938,563. The following are descriptions of illustrative embodiments of such optical core sheets. Preferred optical cores include the embedded-lens and the enclosed-lens optical cores.

The materials of the surface of the optical core to which the vinyl film is laminated can include a wide variety of polymers. Nonlimiting examples include poly(vinyl butyral), aliphatic polyester polyurethane, aliphatic polyether polyurethane, aliphatic polycarbonate polyurethane, ethylene acrylic acid

copolymers, ethylene vinyl acetate copolymers, crosslinked acrylate polymers, and polycarbonate. Preferred polymers of the optical core surface to which the vinyl film is laminated include poly(vinyl butyral) and polyester polyurethane.

A typical "embedded-lens" retroreflective sheeting 10 is illustrated in Fig.

- 5 1. An optical core 17 includes a monolayer of optical elements 11 embedded between transparent bonding and spacing layers 12 and 13, a specularly reflective layer 14, which is typically aluminum vapor-deposited on the spacing layer 13, and a layer of pressure sensitive adhesive 15 covering the reflective layer. A transparent cover film 16, which forms the exterior front surface of the
- 10 sheeting, can be the vinyl film described herein. Light rays incident on the sheeting travel through the layers 16 and 12 to the optical elements 11, which act as lenses focusing the incident light approximately onto the appropriately spaced specularly reflective layer 14. Thereupon the light rays are reflected back out of the sheeting along substantially the same path as they traveled to the sheeting.
- 15 Embedded-lens sheeting as described has the advantage that, because the optical elements are embedded within the sheeting, incident light rays are focused onto the specularly reflective layer irrespective of whether the front of the sheeting is wet or dry.

Specific examples of embedded-lens optical cores are disclosed in U.S.

- 20 Patent Nos. 4,950,525 (Bailey) and 4,511,210 (Tung et al.). For example, the optical elements can be pressed into an extruded thermoplastic aliphatic polyurethane film. Alternatively, an extruded ethylene acrylic acid film can be used in place of the polyurethane film.

A typical "enclosed-lens" retroreflective sheeting 28 is illustrated in Fig.

- 25 2. An optical core sheet (often referred to as a retroreflecting base material) 20 includes a binder layer 21, substantially a monolayer of optical elements 22, a specularly reflective layer 24, and a pressure sensitive adhesive layer 26 covered by a removable liner 27. In this embodiment, the optical elements are substantially fully embedded in the binder layer. A transparent cover film 29,
- 30 which forms the exterior front surface of the sheeting, can be the vinyl film described herein. An example of such sheeting is commercially available from Minnesota Mining and Manufacturing Company ("3M"), St. Paul, MN under the trade designation "Scotchlite Reflective License Plate Sheeting No. 3750".

Another example of a typical "enclosed-lens" retroreflective sheeting 38 is illustrated in Fig. 3. In this embodiment, the optical core 30 includes a binder layer 31, substantially a monolayer of optical elements 32, a specularly reflective layer 34, and a pressure sensitive adhesive layer 36 covered by a removable liner 5 37. In this embodiment, the optical elements are generally embedded about 50 percent in the binder layer. A transparent cover film 39, which forms the exterior front surface of the sheeting, can be the vinyl film described herein.

In the illustrative embodiments shown in Figs. 2 and 3, the thickness of the binder layer typically is about 20 micrometers to about 120 micrometers. It 10 typically includes a crosslinked poly(vinyl butyral) resin or a synthetic polyester resin crosslinked with a butylated melamine resin. The optical elements are typically microspheres made of glass, having refractive indices of about 2.1 to about 2.3, with diameters ranging from about 30 micrometers to about 200 micrometers, preferably averaging about 60 micrometers in diameter. The 15 reflective material may be a layer of metal flakes or vapor or chemically deposited metal layer such as aluminum or silver. As such, the sheeting will have a silver or gray appearance caused by the metallic appearance of the reflective material. However, colored sheeting can be prepared by placing dyes or pigments, which are preferably light transmissible, in the spacing layer, bead 20 bond layer, cover film, and/or primer layers.

Alternative embodiments of "enclosed-lens" retroreflective sheeting include a bead bond layer and a space coat layer in place of the binder layer illustrated in Figs. 2 and 3. The reflective layer is held in a cooperative position with respect to the optical elements by the space coat layer. That is, the optical 25 elements have a first hemispherical portion enclosed by the bead bond and a second opposing hemispherical portion spaced at the cooperative position from the reflective coating by the space coat layer. The space coat layer typically has a thickness extending from the surface of the microspheres approximately one fourth the average diameter of the microspheres. An example of such an optical 30 core is disclosed in the context of a license plate in U.S. Pat. No. 5,882,771 (Klein et al.).

Fig. 4 illustrates an "encapsulated-lens" retroreflective article 48. An optical core sheet 40 includes transparent beads 41 having a first hemispherical



air exposed portion, and a second opposing hemispherical portion having the reflective coating 44 thereon. A sealing member 46, having a second major surface 45 opposed from the viewing surface 43, is bonded to portions of the cover film 49 to form a pattern of seal legs (such as the ones shown as 42),  
5 wherein the cover film 49, the sealing member 46, and the seal legs 42 form a plurality of encapsulated air cells 47, with the cover film 49 in spaced relation to the sealing member 46, and the air-exposed portions of the beads within the cells.

The bonding portions between the face member and sealing member  
10 form seal legs. These legs have a height sufficient to provide an air interface for the unbonded portion of the face member. The seal legs may be formed, for example, by application of heat and pressure to the sealing member and the cover film as disclosed in U.S. Pat. No. 3,190,178 (McKenzie). In this embodiment, the seal legs may form a sealing pattern of individual air-tight cells each having a  
15 small area on the viewing surface 43. Seal legs may also be called sealing walls, bonds, bond lines, septa, or seal leg members, which for the purposes of this application are all equivalent terms.

Fig. 5a illustrates a reflector-coated prismatic-type retroreflective article  
50 having a cover film 52 (the vinyl film described herein) with a major viewing  
20 surface 53, and a retroreflective member 54. The retroreflective member 54 has a first major surface in contact with the face member and a second opposing microstructured surface having retroreflective elements 56, such as prisms, with a reflective coating thereon.

The total thickness of retroreflective members having cube corner  
25 retroreflective elements is typically between about 0.2 mm and 0.7 mm, but may be more or less depending on the polymers used. As the thickness of the retroreflective member decreases, the flexibility of the member may also be expected to increase.

Polymers are selected for the retroreflective member 54 in view of the  
30 properties desired of the resultant article, the methods used for forming the retroreflective surface, the desired bondability to the sealing member, and the nature of any other members of the retroreflective article. Polymers selected for the microstructured layer preferably should form cube corner elements that are

dimensionally stable so that precise geometry desired for retroreflection is maintained. The polymeric materials selected for the microstructured surface tend to be relatively inflexible, hard, and rigid materials with a high Vicat softening temperature relative to other polymers. Thus, these polymers may be brittle or easily fractured when at room temperature or lower temperatures. Notably, however, many of these polymers retain their transparency and their shape under adverse conditions. Suitable polymers include thermoplastic or thermosetting materials, as desired. The polymer forming the retroreflective surface preferably is substantially optically clear, though it may be colored as desired. These polymers are often selected for one or more of the following reasons: thermal stability, dimensional stability, environmental stability, clarity, excellent release from the tooling or mold, and capability of receiving a reflective coating.

Suitable microstructured surfaces include, for example, cube corner elements that can be of various geometric designs. The optical elements may also be called cube corners, prisms, microprisms, or triple mirrors, which for the purposes of this application are all equivalent terms. The basic cube corner retroreflective element is generally a tetrahedral structure having, for example, a base triangle and three mutually substantially perpendicular optical faces that cooperate to retroreflect incident light. The optical faces preferably intersect at an apex, with the base triangle lying opposite the apex. Each cube corner element also has an optical axis, which is the axis that extends through the cube corner apex and trisects the internal space of the cube corner element. Light incident on the first major viewing surface enters the base triangle and is transmitted into the internal space of the cube, is reflected from each of the three optical faces, and is redirected back in the same general direction as the incoming incident light. It is optional whether the faces of the cubes are exposed to an air interface or coated with a reflective coating, such as aluminum. Fig. 5a illustrates a microstructured surface that is spectrally coated with metal or other suitable reflective coatings as a means for altering the optical performance of the retroreflective member. In this embodiment, an optional sealing member (not shown) may be in complete contact with the microstructured surface without loss in retroreflection.

The height of the cube corner elements, defined as the length of the optical axis, is preferably as small as manufacturable for ease of sealing but may be as large as necessary while recognizing the desirability of avoiding waste of material and of increasing the thickness of the article. The minimum height is preferably about 0.01 mm and the maximum height is preferably less than 1 mm. The height of the cube elements is more preferably 0.02 mm to 0.5 mm. This microstructured surface is molded to yield a cube layer using any of a variety of techniques known to those skilled in the art.

Fig. 5b illustrates an enclosed prismatic-type retroreflective article 50 having a cover film 52 with a major viewing surface 53, and a retroreflective member 54. The retroreflective member 54 has a first major surface in contact with the face member and a second opposing microstructured surface having retroreflective elements 56, such as prisms, with a reflective coating thereon. An underlying layer 55 lies against the reflective coating, thereby enclosing the prisms. The face member preferably comprises a transparent multilayer film, as previously discussed for Fig. 5a.

Fig. 6 illustrates a cross-sectional view of an encapsulated prismatic-type retroreflective article 60 having a cover film 62 with major viewing surface 63, retroreflective member 64 with retroreflective elements 56 forming a microstructured surface, and sealing member 66 having a major surface 67. The sealing member 66 is bonded to the microstructured surface or to the retroreflective member 64 to form seal legs (42 in Fig. 6). The microstructured surface, the sealing member, and the seal legs form a plurality of encapsulated air cells 65.

Typically, the seal legs have a height sufficient to provide an air interface for the unbonded portion of the microstructured surface. The width of the seal legs suitably may vary between about 0.2 mm to 4 mm, preferably between about 0.4 mm to 1 mm, and most preferably is at a width sufficiently narrow to maximize retroreflectivity while maintaining a satisfactory bonding strength of the sealing member to the microstructured surface. The seal legs may be formed by application of heat and pressure to the retroreflective member and the sealing member as disclosed in U.S. Pat. No. 3,190,178 (McKenzie).

The thickness of the sealing member is sufficient to protect the microstructured surface from exposure to factors, such as dirt and water that lower their optical efficiency and to bond the article to a substrate. The thickness of the sealing member is preferably at least 0.02 mm, more preferably at least 0.06 mm, but generally the thickness does not exceed about 0.3 mm.

The seal legs typically form a sealing pattern on the viewing surface of the face member. Patterns, such as hexagonal, rectangular, square, circular, hexagonal, or chain link, may be employed as desired. The seal legs do not retroreflect as much light as the area within the cells, which results in the pattern on the viewing surface. Typically, each individually sealed air cell has length and width dimensions A and B. Dimension A and B preferably range from about 4 mm to about 50 mm. Dimensions A and B determine the area of each cell on the viewing surface. The area of the cells is preferably small. For example, the surface area of each cell is less than 5 square centimeters, preferably less than 4 centimeters, more preferably less than 1 square centimeters, and most preferably less than 0.5 square centimeters, although area may vary from cell to cell. Dimensions of a cell may be measured using a metric ruler and the area of a cell calculated by formulas known to those skilled in the art.

Some illustrative examples of materials for the sealing member include thermoplastic, heat-activated, ultraviolet cured, and electron beam cured polymer systems. Preferably, the Vicat softening temperature of the sealing member is at least about 30°C less than that of the microstructured surface.

Other optical cores can include raised-ridge prismatic-type retroreflective articles having a pattern of raised ridges with retroreflective elements forming a microstructured surface on the retroreflective member.

### **Optional Graphics**

Optionally, graphics can be applied to the optical core or the vinyl film before the primer is applied and before lamination of the optical core and vinyl film. When images are embedded in this way within the sheeting, the images are generally more durable. Such images can be formed using gravure coating, for example. Alternatively, images can be formed in the reflective layer of an

optical core sheet through the use of lasers as disclosed in U.S. Pat Nos. 4,634,220 (Hicks et al.) and 4,688,894 (Hockert).

If graphics are applied using commercially available inks, such as vinyl-based inks, a primer can optionally be used between the graphics and the optical core or vinyl film. The primer described herein, optionally crosslinked with, for example, an aziridine crosslinker (such as that commercially available from Zeneca, Wilmington, MA under the trade designation "Neocryl CX-100") can be used. Other inks, such as EAA-based inks, can be used with a primer that includes a copolymer of an olefinic monomer and a second monomer containing a pendant carboxylic group described herein, either alone or mixed with the urethane polymer described herein. Other suitable covalent crosslinkers are described in U.S. Patent No. 5,468,532 (Ho et al.).

#### **Methods of Making Sheeting**

Methods of making the sheeting of the present invention (preferably, retroreflective sheeting) involve laminating a vinyl film to a preformed optical core. The vinyl film, the preformed optical core, or both are primed with a primer that includes a urethane primer before laminating them together.

In one preferred embodiment, a method is provided that includes: providing a vinyl film that includes a primer disposed on a first major surface thereof to form a primed surface, wherein the primer includes a urethane polymer; providing a preformed optical core having two major surfaces; and laminating a first major surface of the preformed optical core to the primed surface of the vinyl film. In this method, the vinyl film can be primed with a urethane polymer provided from a water-based urethane resin or from a solvent-based urethane resin.

In another preferred embodiment, a method is provided that includes: providing a vinyl film having two major surfaces; providing a preformed optical core that includes a primer disposed on a first major surface thereof to form a primed surface, wherein the primer includes a urethane polymer; and laminating a first major surface of the vinyl film to the primed surface of the preformed optical core. In this method, the optical core is preferably primed with a urethane polymer provided from a water-based urethane resin.

The optical core sheet and vinyl film, at least one of which is primed with a urethane polymer-containing primer, can be directly laminated together using a typical thermal/mechanical method. Typically, the lamination temperature is sufficiently hot to thermally bond the optical core to the vinyl film. Typically, 5 opposing nip rolls are used, which may both be smooth, or one may be smooth and one embossed for the formation of the seal legs described in certain of the desired embodiments disclosed herein. In addition to thermoforming techniques, other techniques, such as ultrasonic welding, radio frequency welding, thermal fusion, and reactive welding, may be used.

10 In a preferred lamination process, the application of temperature and pressure occurs through the use of a nip roll process. Typically, the nip force is about 17 kg/cm width to about 21 kg/cm width; the hot can temperature is about 140°C to about 200°C; and the line speed is about 5 meters/minute to about 50 meters/minute. Those skilled in the art will optimize the line speed, nip force 15 and other lamination conditions (e.g., hot can temperature) to obtain the desired properties in finished laminated sheeting, preferably retroreflective sheeting, of the invention.

Prior to the lamination process, it may be desirable to apply an adhesion-promoting treatment to the surface of the optical core sheet and/or vinyl film. 20 This can include a corona or plasma treatment. Such treatment is typically applied to the surface of the optical core and/or vinyl film and then optionally the primer is applied to the treated surface.

### **Products**

25 The sheeting of the present invention can be used in a variety of products, including, but not limited to, a license plate, a reflective graphic article (e.g., traffic sign), a pavement marking article, a road sign, vehicle conspicuity sheeting, an article of clothing (e.g., a warning vest), footwear (e.g., running shoes), an accessory bag, a backpack, a protective cover, a sheet, a tarpaulin 30 (e.g., a truck trailer cover), a warning tape, a decorative webbing, a structural webbing, or tapes, piping, patches and emblems for attachment to such items.

In many applications, the retroreflective article having a vinyl film is mounted via an adhesive to a rigid substrate, such as an aluminum plate for a

highway sign or for a license plate, or to a highway surface, such as concrete or asphalt. Typically, for signage and license plates, the vinyl film forms the outermost surface of each of the articles.

An exemplary license plate in which the vinyl cover film and primer of the present invention could be used is described in U.S. Pat. No. 5,882,771, which includes a substrate (e.g., metal or plastic) having characters embossed therein and a retroreflective sheeting adhered thereto. An exemplary graphics article in which the vinyl film and primer of the present invention could be used is a roll-up sign, which includes a vinyl film mounted on a flexible scrim-reinforced backing, as disclosed in U.S. Pat. Application Serial No. 09/393,369 (Atty. Docket No. 55056 USA 2A), filed on September 10, 1999, entitled "Retroreflective Articles Having Multilayer Films and Methods of Manufacturing Same." Exemplary pavement marking articles or other traffic control articles in which the vinyl cover film and primer of the present invention could be used are disclosed in U.S. Pat. No. 5,981,033 (Haunschild et al.) and International Publication Nos. WO 98/40562, WO 97/01677, and WO 97/01678. For example, the vinyl film and primer of the present invention can be used with conventional optical core sheets used in: vertical applications, such as on Jersey barricades or guard rails; curved surface applications, such as traffic barrels, tubes, and cones; vehicle surfaces; road surfaces; signage; license plates; reflective graphics; etc.

### Examples

Features and advantages of the invention are further explained in the following illustrative examples. All parts and percentages herein are by weight unless otherwise specified. The constructions cited in the Examples and Comparative Examples were evaluated by the following tests.

#### 180° Peel Force Test

The peel force was performed on each laminated construction on a test panel by clamping the panel in the lower jaw of a Sintech 1 tensile testing apparatus (MTS, Eden Prairie, MN) and the filament tape tab of the laminated construction in the upper jaw. The laminated construction was separated at a

180° peel back angle using a crosshead speed of 30.5 cm/minute. The peel force was recorded in grams/cm (lb/in) or, if the vinyl film could not be peeled apart from the remainder of the laminated construction, rated as "Could Not Be Separated (CS)."

5

## EXAMPLES 1 – 2

### Peel Force Between Primed Enclosed-Lens Optical Core and Unprimed Vinyl Film

A first construction was made by casting 0.06 mm (2.5 mil) thick vinyl  
10 film from organosol on a polyester (PET) carrier prepared according to Example 5 of U.S. Pat. No. 5,874,158 (Ludwig et al.), except that no pigments were added and an acrylic resin commercially available under the trade designation "Elvacite 2013" from DuPont was substituted for "Acryloid B66" acrylic resin.

A second construction consisted of an enclosed-lens optical core  
15 commercially available from Minnesota Mining and Manufacturing Company ("3M"), St. Paul, MN under the trade designation "Scotchlite Reflective License Plate Sheeting No. 3750." The surface of the optical core was corona treated in an air atmosphere at 1.4 kilowatts per meter width. Each corona treated optical core construction was independently coated with a primer solution prepared by  
20 combining the primer listed in TABLE I with a 0.05 wt-% wetting agent (i.e., surfactant) commercially available from Air Products, Allentown, PA under the trade designation "Surfynol 104 PA" to provide a primer solution of 99.95:0.05 (by weight).

The primer solution was coated on the optical core using a #8 wire bar to  
25 provide a 0.018 mm (0.72 mil) wet coating thickness. The primer was dried for 5 minutes in a 121°C (250°F) oven.

The exposed surfaces of both the primed optical core and the unprimed vinyl film were air corona treated as described above for the optical core. A 5.1 cm wide by 25.4 cm long strip of green tape commercially available from 3M  
30 under the trade designation "3M #8402" was placed crossweb between the first and second constructions and aligned with both edges of the constructions. The two constructions with the green tape therebetween were laminated together at 9.1 meters per minute using a hot can surface temperature of 154°C (310°F).



The resultant laminated constructions were stored at room temperature for about 24 hours.

The PET carrier on the vinyl film was removed and then a razor blade was used to cut the laminated construction down the center of the green tape to form two portions. From one portion of the laminated construction was cut a 2.5 cm wide by 12.7 cm long strip, the strip having the green tape on one edge. The release liner was removed from the adhesive of the optical core portion of the construction (i.e., the second construction). The exposed adhesive surface of the strip was applied to a 7 cm wide by 28 cm long aluminum panel (6061T6 alloy with etch and desmut surface from Q Panel Company, Cleveland, OH) aligning the edge of the green tape portion of the strip with the edge of the aluminum panel. The strip was applied to the panel by running a rubber coated, 5 cm wide roller back and forth along the length of the strip twice using hand pressure.

The vinyl film was lifted from the remainder of the laminated construction in the area of the green tape area and a strip of filament tape commercially available from 3M under the trade designation "Scotch 898 Tape," 2.5 cm wide by 20 cm long, was wrapped around and adhered to the vinyl film in the area of its separation from the remainder of the construction (i.e., at the area of the green tape) to form a tab of about 10 cm in length. The Peel Force Test was performed immediately to provide the peel force data in TABLE I.

The 180° Peel Force Test data in TABLE I show that a strong bond was formed between the primed optical core and the unprimed vinyl film. The peel force between the primed optical core and the unprimed vinyl film was of such high strength that the optical core broke, i.e., the two constructions could not be separated.

TABLE I

Ex. No.	Primer (w/w solution ratio)	Primer (w/w solid ratio)	Peel Force (g/cm; lb/in)
1	100 % Neorez 972 <sup>1</sup>	----	CS
2	Neorez 972/Michem 4983R <sup>2</sup> (30/70)	36.7/63.3	CS

- 1 A 34 wt-% solids dispersion of polyurethan in water commercially available from Avecia (Formerly Zeneca Resins), Wilmington, MA under the trade designation "Neorez 972."
- 2 A 25 wt-% solids dispersion of EAA commercially available from Michelman Inc., Cincinnati, OH under the trade designation "Michem 4983R."
- 3 CS = Could Not Be Separated.

10

**EXAMPLES 3 – 6**

Peel Force Between Primed Vinyl Film and  
Unprimed Enclosed-Lens Optical Core

15 The constructions of Examples 3-6 were prepared as detailed for Examples 1-2 with the exception that the primer solutions (prepared by combining the primer listed in TABLE II with 0.05% "Surfynol 104PA" surfactant to provide a primer solution of 99.95:0.05 (by weight)) were independently coated on the vinyl film instead of the optical core.

20 For Example 5, a second coat of primer solution was applied atop the first coat after the first coat was dried. The second coat of primer solution consisted of "Michem 4983R" EAA dispersion and "Surfynol 104PA" surfactant in a 99.95:0.05 weight ratio. The application, wet coating thickness and drying conditions of the second coat were the same as that described for the first coat.

25 First and second constructions were prepared, air corona treated, laminated together, sample laminated constructions prepared as described in Examples 1-2 and tested according to the 180° Peel Force Test. The Peel Force Test values are provided in TABLE II.

The 180° Peel Force Test data in TABLE II show that a strong bond was formed between the primed vinyl film and the unprimed optical core. The peel force between the primed vinyl film and the unprimed optical core was of such high strength that the optical core broke, i.e., the two constructions could not be separated.

TABLE II

Ex. No.	Primer First Coat	Primer Second Coat	Peel Force (g/cm; lb/in)
3	100 % Neorez 972	No	CS
4	Neorez 972/Michem 4983R (30/70)	No	CS
5	100% Neorez 972	Michem 4983R diluted with 0.05% Surfynol 104PA	CS
6	QC4820*	No	CS

\* An aliphatic polyester urethane diluted to 12 wt-% with 1:1 (wt. ratio) xylene/ethanol commercially available from K. J. Quinn & Co., Inc., Seabrook, NH under the trade designation "QC4820."

### EXAMPLES 7 - 8

#### Peel Force Between Primed Embedded-Lens Optical Core and Unprimed Vinyl Film

The constructions of Examples 7-8 were prepared as detailed for Examples 1-2 with the exception that an embedded-lens optical core was substituted for the enclosed-lens optical core. The embedded-lens optical core was prepared according to Example 2 of U.S. Pat. No. 4,511,210 (Tung et al.).

First and second constructions were prepared, air corona treated, laminated together, sample laminated constructions prepared as described in Examples 1-2 and tested according to the 180° Peel Force Test. The Peel Force Test values are provided in TABLE III.

The Peel Force Test data in TABLE III show that the peel force between the primed optical core and the unprimed vinyl film was high and provided constructions that did not easily peel apart.

5

TABLE III

Ex. No.	Primer (w/w solution ratio)	Primer (w/w solid ratio)	Peel Force (g/cm; lb/in)
7	100 % Neorez 972	----	981; 5.5
8	Neorez 972/Michem 4983R (30/70)	36.7/63.3	998; 5.6

**EXAMPLES 9 – 11**Peel Force Between Primed Vinyl Film and

10

Unprimed Embedded-Lens Optical Core

The constructions of Examples 9-11 were prepared as detailed for Examples 3-6 with the exception that an embedded-lens optical core was substituted for the enclosed-lens optical core. The embedded-lens optical core was prepared according to Example 2 of U.S. Pat. No. 4,511,210 (Tung et al.).

15

First and second constructions were prepared, air corona treated, laminated together, sample laminated constructions prepared as described in Examples 1-2 and tested according to the 180° Peel Force Test. The Peel Force Test values are provided in TABLE IV.

The Peel Force Test data in TABLE IV show that the peel force between the primed vinyl film and the unprimed optical core was high and provided constructions that did not easily peel apart.

TABLE IV

Ex. No.	Primer (w/w solution ratio)	Primer (w/w solid ratio)	Peel Force (g/cm; lb/in)
9	100 % Neorez 972	----	1159; 6.5
10	Neorez 972/Michem 4983R (30/70)	36.7/63.3	1017; 5.7
11	QC4820 diluted to 12 wt-% with 1:1 (wt. ratio) xylene/ethanol	----	1213; 6.8

5

**EXAMPLES 12 -13**

Peel Force Between Primed Vinyl Film and  
Unprimed Embedded-Lens Optical Core

The constructions of Examples 12-13 were prepared as detailed for Examples 3-6 with the exception that an embedded-lens optical core was substituted for the enclosed-lens optical core. Then embedded-lens optical core was prepared according to Example 1 of U.S. Pat. No. 4,950,525 with the exception that "Primacor 3440" (ethylene acrylic acid resin from Dow Chemical, Midland, MI) instead of aliphatic polyurethane was used to extrude the film.

First and second constructions were prepared, air corona treated, laminated together, sample laminated constructions prepared as described in Examples 1-2, except that all the corona treatments were conducted in an air atmosphere at 0.2 kilowatts per meter width and the first and second constructions were laminated together at 1.5 meters per minute using a hot can surface temperature of 157°C (315°F). The test samples were tested according to the 180° Peel Force Test and the values provided in TABLE V.

The Peel Force Test data in TABLE V show that the peel force between the primed vinyl film and the unprimed optical core was high and provided constructions that did not easily peel apart.

TABLE V

Ex. No.	Primer (w/w solution ratio)	Primer (w/w solid ratio)	Peel Force (g/cm; lb/in)
12	100 % Neorez 972	----	838; 4.7
13	Neorez 972/Michem 4983R (30/70)	36.7/63.3	820; 4.6

**COMPARATIVE EXAMPLE A**

5

Peel Force Between Unprimed Vinyl Film and  
Unprimed Enclosed-Lens Optical Core

The construction of Comparative Example A was prepared as detailed for Examples 1-2 with the exception that the enclosed-lens optical core was not primed.

10

First and second constructions were prepared, air corona treated, laminated together, a sample laminated construction prepared as described in Examples 1-2 and tested according to the 180° Peel Force Test. The Peel Force Test value was 53.5 g/cm (0.3 lb/in).

15

**COMPARATIVE EXAMPLE B**

Peel Force Between Unprimed Vinyl Film and  
Unprimed Embedded-Lens Optical Core

The construction of Comparative Example B was prepared as detailed for Examples 7-8 with the exception that the embedded-lens optical core was not primed.

20

First and second constructions were prepared, air corona treated, laminated together, a sample laminated construction prepared as described in Examples 1-2 and tested according to the 180° Peel Force Test. The Peel Force Test value was 410.2 g/cm (2.3 lb/in).

25

The complete disclosure of all patents, patent documents, and publications are incorporated herein by reference as if individually incorporated. Various modifications and alterations of this invention will become apparent to

those skilled in the art without departing from the scope and spirit of this invention.

**WHAT IS CLAIMED IS:**

1. A sheeting comprising:  
a vinyl film having two major surfaces;  
5 a preformed optical core laminated to a first major surface of the vinyl film;  
a primer disposed between the vinyl film and the preformed optical core, wherein the primer comprises a urethane polymer; and  
optionally, graphics positioned between the primer and the optical core or  
10 the primer and the vinyl film.
2. The sheeting of claim 1 wherein the primer comprises a layer having a thickness of no greater than about 12.5 micrometers.
- 15 3. The sheeting of claim 1 which is a retroreflective sheeting.
4. The sheeting of claim 1 wherein the primer is formed from a water-based urethane resin or a solvent-based urethane resin.
- 20 5. The sheeting of claim 1 wherein the primer further comprises a copolymer comprising an olefinic monomer and a second monomer comprising a pendant carboxyl group.
6. The sheeting of claim 5 wherein the copolymer is an ethylene/acrylic acid  
25 copolymer.
7. The sheeting of claim 6 wherein the ethylene/acrylic acid copolymer is mixed with the urethane polymer.
- 30 8. The sheeting of claim 7 wherein the mixture forms a first layer proximate the vinyl film and the primer further comprises a second layer comprising an ethylene/acrylic acid copolymer.



9. The sheeting of claim 8 wherein the second layer further comprises a urethane polymer mixed with the ethylene/acrylic acid copolymer.
10. The sheeting of claim 7 wherein the ethylene/acrylic acid copolymer is present in an amount of about 7 wt-% to about 87 wt-%, based on polymer solids.
11. The sheeting of claim 10 wherein the urethane polymer is present in an amount of about 13 wt-% to about 93 wt-%, based on polymer solids.
12. The sheeting of claim 1 wherein the optical core comprises an embedded-lens optical core or an enclosed-lens optical core.
13. A sheeting comprising:  
a vinyl film having two major surfaces;  
a preformed optical core laminated to a first major surface of the vinyl film;  
a primer disposed between the vinyl film and the preformed optical core, wherein the primer consists essentially of a urethane polymer; and  
optionally, graphics positioned between the primer and the optical core or the primer and the vinyl film.
14. The sheeting of claim 13 wherein the primer comprises a layer having a thickness of no greater than about 12.5 micrometers.
15. The sheeting of claim 13 which is a retroreflective sheeting.
16. A sheeting comprising:  
a vinyl film having two major surfaces;  
a preformed optical core laminated to a first major surface of the vinyl film;  
a primer disposed between the vinyl film and the preformed optical core, wherein the primer comprises a first layer comprising a urethane polymer

proximate the vinyl film and a second layer comprising an ethylene/acrylic acid copolymer; and

optionally, graphics positioned between the primer and the optical core or the primer and the vinyl film.

5

17. The sheeting of claim 16 wherein the primer comprising the first and second layers has a thickness of no greater than about 12.5 micrometers.

18. The sheeting of claim 16 wherein the first layer further comprises an  
10 ethylene/acrylic acid copolymer mixed with the urethane polymer.

19. The sheeting of claim 18 wherein the second layer further comprises a urethane polymer mixed with the ethylene/acrylic acid copolymer.

15 20. The sheeting of claim 16 which is a retroreflective sheeting.

21. A sheeting comprising:  
a vinyl film having two major surfaces;  
a preformed optical core laminated to a first major surface of the vinyl  
20 film;  
a primer disposed between the vinyl film and the preformed optical core,  
wherein the primer is formed from a solvent-based urethane resin; and  
optionally, graphics positioned between the primer and the optical core or the primer and the vinyl film.

25

22. A retroreflective sheeting comprising:  
a vinyl film having two major surfaces;  
a preformed optical core laminated to a first major surface of the vinyl  
film;

30 a primer disposed between the vinyl film and the preformed optical core at a thickness of no greater than about 12.5 micrometers, wherein the primer comprises a urethane polymer; and

optionally, graphics positioned between the primer and the optical core or the primer and the vinyl film.

23. A license plate comprising the sheeting of claim 1.
- 5
24. A reflective graphic article comprising the sheeting of claim 1.
25. A pavement marking comprising the sheeting of claim 1.
- 10 26. A method of making sheeting comprising:  
providing a vinyl film comprising a primer disposed on a first major surface thereof to form a primed surface, wherein the primer comprises a urethane polymer;  
providing a preformed optical core having two major surfaces; and  
15 laminating a first major surface of the preformed optical core to the primed surface of the vinyl film.
27. The method of claim 26 wherein providing a vinyl film comprising a primer comprises providing a vinyl film having two major surfaces and coating a  
20 water-based urethane resin on a first major surface of the vinyl film.
28. The method of claim 27 wherein providing a vinyl film comprising a primer comprises providing a vinyl film having two major surfaces and coating a solvent-based urethane resin on a first major surface of the vinyl film.
- 25
29. The method of claim 27 further comprising applying graphics to the first major surface of the preformed optical core prior to laminating.
30. The method of claim 27 wherein the sheeting is retroreflective sheeting.
- 30
31. The method of claim 27 wherein the primer further comprises an ethylene/acrylic acid copolymer.

32. The method of claim 31 wherein the ethylene/acrylic acid copolymer is mixed with the polymer comprising the urethane and/or urea groups.
33. The method of claim 32 wherein the mixture forms a first layer proximate the vinyl film and the primer further comprises a second layer comprising a urethane polymer.
34. The method of claim 33 wherein the second layer further comprises an ethylene/acrylic acid copolymer mixed with the urethane polymer.
35. The method of claim 26 wherein the primer comprises a first layer comprising a urethane polymer proximate the vinyl film and a second layer comprising an ethylene/acrylic acid copolymer.
36. The sheeting of claim 35 wherein the first layer further comprises an ethylene/acrylic acid copolymer mixed with the urethane polymer.
37. The sheeting of claim 36 wherein the second layer further comprises a urethane polymer mixed with the ethylene/acrylic acid copolymer.
38. The method of claim 26 wherein the optical core further comprises a binder.
39. A method of making sheeting comprising:  
providing a vinyl film having two major surfaces;  
providing a preformed optical core comprising a primer disposed on a first major surface thereof to form a primed surface, wherein the primer comprises a urethane polymer; and  
laminating a first major surface of the vinyl film to the primed surface of the preformed optical core.
40. The method of claim 39 wherein providing a preformed optical core comprising a primer comprises providing a preformed optical core having two

major surfaces and coating a water-based urethane resin on a first major surface of the optical core.

41. The method of claim 39 wherein the sheeting is retroreflective sheeting.

5

42. The method of claim 39 wherein the primer further comprises an ethylene/acrylic acid copolymer.

43. The method of claim 42 wherein the ethylene/acrylic acid copolymer is mixed with the urethane polymer.

10

44. The method of claim 43 wherein the mixture forms a first layer proximate the optical core and the primer further comprises a second layer comprising a urethane polymer.

15

45. The method of claim 44 wherein the second layer further comprises an ethylene/acrylic acid copolymer mixed with the urethane polymer.

46. The method of claim 39 wherein the primer comprises a first layer comprising a urethane polymer proximate the optical core and a second layer comprising a urethane polymer.

20

47. The method of claim 46 wherein the first layer further comprises an ethylene/acrylic acid copolymer mixed with the urethane polymer.

25

48. The method of claim 46 wherein the second layer further comprises an ethylene/acrylic acid copolymer mixed with the urethane polymer.

49. The method of claim 39 wherein the vinyl film includes a primer disposed on a first major surface thereof to form a primed surface, wherein the primer comprises a urethane polymer; and

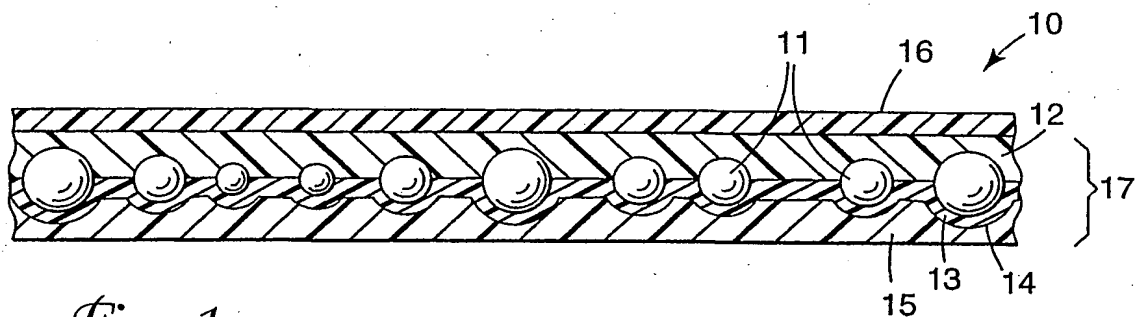
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laminating the primed surface of the vinyl film to the primed surface of the preformed optical core.

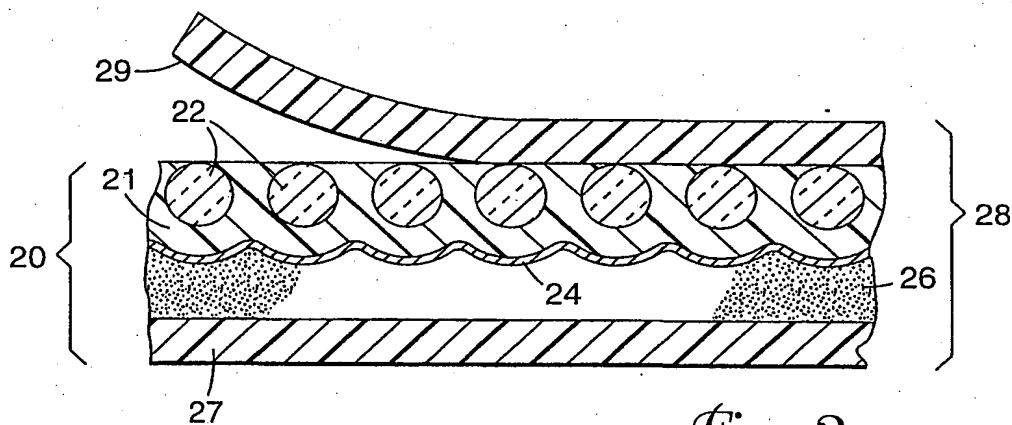
50. The method of claim 39 further comprising applying graphics to the first major surface of the vinyl film prior to laminating.

5

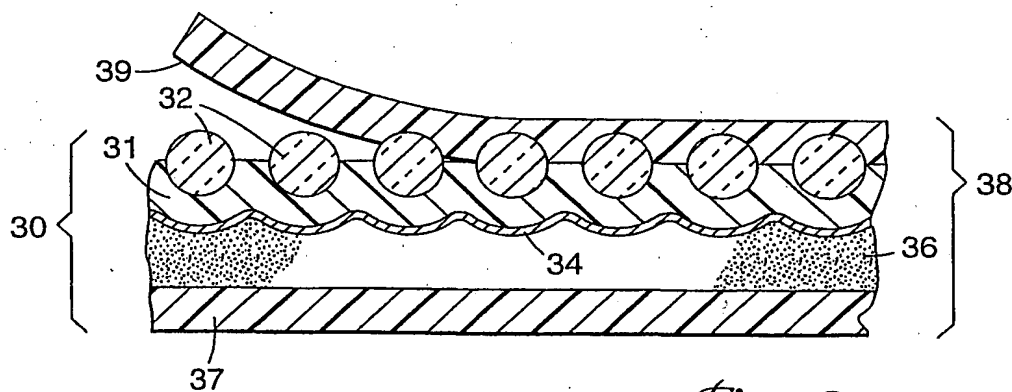
1/2



*Fig. 1*

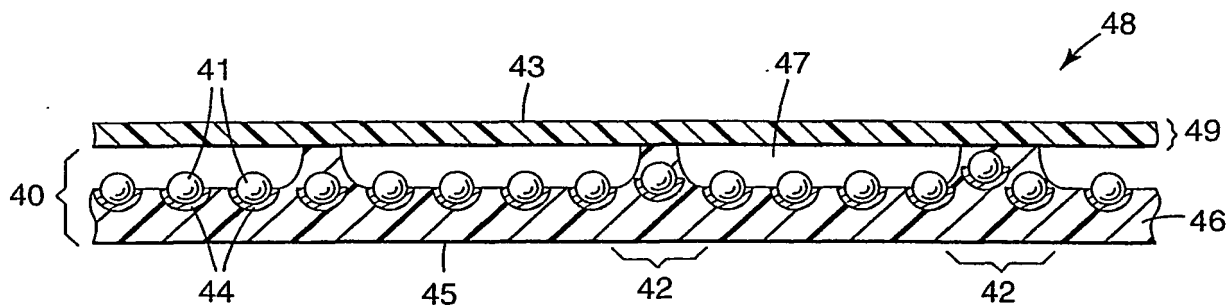


*Fig. 2*

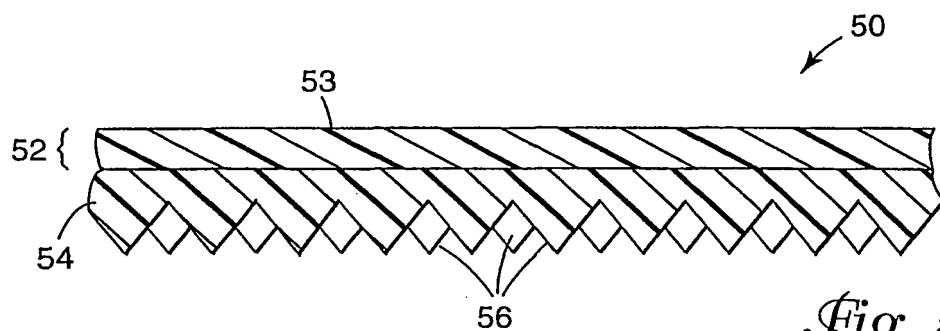


*Fig. 3*

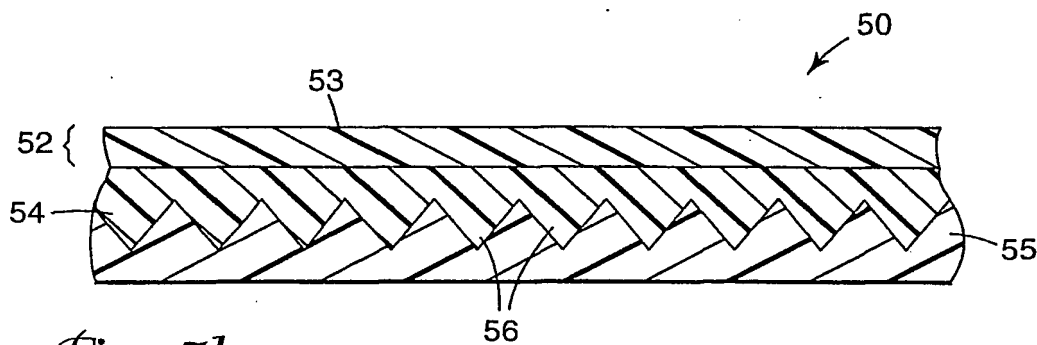
2/2



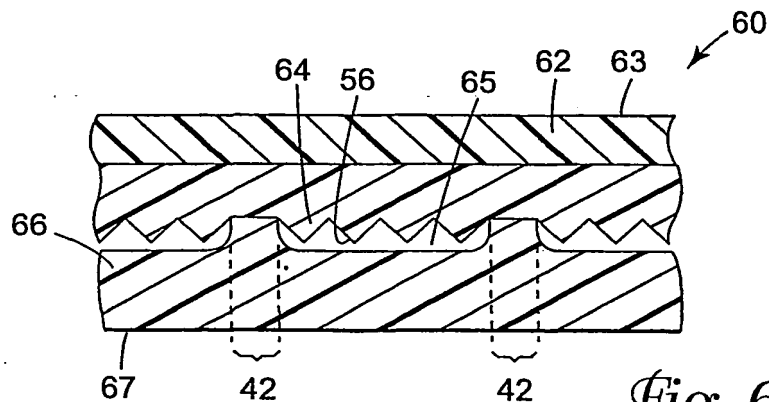
*Fig. 4*



*Fig. 5a*



*Fig. 5b*



*Fig. 6*



## INTERNATIONAL SEARCH REPORT

Int. Patent Application No.

PCT/US 00/24363

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 G02B5/128 B32B17/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G02B B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 393 590 A (CASPARI RUEDIGER) 28 February 1995 (1995-02-28) column 4, line 7 -column 7, line 60; figure 2	1-50
X	US 5 620 775 A (LAPERRE JAMES D) 15 April 1997 (1997-04-15)  column 13, line 13 -column 15, line 45 column 19, line 25 -column 20, line 28; figures 11-13	1, 3-7, 12, 13, 15, 16, 18, 21-32, 38-43, 49, 50



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 5 882 771 A (KLEIN DEANA A ET AL) 16 March 1999 (1999-03-16)</p> <p>column 4, line 5 - line 39 column 8, line 52 -column 9, line 48 column 11, line 48 -column 12, line 45; figure 4</p>	1,13,16, 21,22, 26,39
A	<p>WO 96 19543 A (MINNESOTA MINING &amp; MFG) 27 June 1996 (1996-06-27) page 5, line 3 -page 9, line 7 page 18, line 10 -page 20, line 16; figure 1</p>	1-50
A	<p>US 4 605 592 A (FALAAS DENNIS O ET AL) 12 August 1986 (1986-08-12)</p> <p>column 2, line 3 -column 4, line 15; figure 1</p>	1,7-11, 13, 16-19, 21,22, 26, 33-37, 39,44-50
A	<p>US 5 019 440 A (OGASAWARA YASUKICHI ET AL) 28 May 1991 (1991-05-28)</p> <p>column 2, line 67 -column 5, line 55; figure 1</p>	1,13,16, 21,22, 26,39

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